

# Canonical Transformation Approach to the Ultrafast Non-linear Optical Dynamics of Semiconductors

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## Abstract

We develop a theory describing the effects of many-particle Coulomb correlations on the coherent ultrafast nonlinear optical response of semiconductors and metals. Our approach is based on a mapping of the nonlinear optical response of the “bare” system onto the linear response of a “dressed” system. The latter is characterized by effective time-dependent optical transition matrix elements, electron/hole dispersions, and interaction potentials, which in undoped semiconductors are determined by the single-exciton and two-exciton Green functions in the absence of optical fields. This mapping is achieved by eliminating the optically-induced charge fluctuations from the Hamiltonian using a Van Vleck canonical transformation. It takes into account all many-body contributions up to a given order in the optical fields as well as important Coulomb-induced quantum dynamics to all orders in the optical field. Our approach allows us to distinguish between optical nonlinearities of different origins and provides a physically-intuitive interpretation of their manifestations in ultrafast coherent nonlinear optical spectroscopy.

## I. INTRODUCTION

In semiconductors and metals, the Coulomb interactions among electrons and holes strongly affect the optical spectra close to the onset of absorption.<sup>1</sup> In undoped semiconductors, the  $e$ - $h$  attraction leads to exciton resonances, while in doped quantum wells and metals it leads to the Fermi-Edge-Singularity.<sup>2</sup> In the vicinity of the resonances, the interactions between photoexcited  $e$ - $h$  pairs and Fermi sea electrons also affect strongly the time-dependence of the  $e$ - $h$  polarization measured in ultrafast nonlinear optics experiments. This allows one to obtain new information on many-body correlations, not easily accessible with other experimental techniques, by using transient pump-probe and wave-mixing spectroscopy.<sup>3</sup> The interpretation of such experiments, however, requires solving a challenging time-dependent many-body problem. Indeed, during femtosecond time scales, the Coulomb interactions dominate the time-dependence of the experimentally-measurable polarization. In the coherent limit, the standard quasi-equilibrium approaches no longer apply. This led to the development of alternative approximations for undoped semiconductors. The most important of those is the Semiconductor Bloch Equations (SBE's) approach, which treats exciton-exciton interaction effects on the nonlinear optical response within the Hartree-Fock approximation.<sup>4,5</sup>

Recent experiments, however, revealed pronounced features in the amplitude and phase dynamics of the nonlinear polarizations that could not be captured by the SBE's.<sup>6</sup> In Ref. 7, for example, pronounced features in the phase and amplitude dynamics of the four-wave-mixing polarization were attributed to non-Markovian dephasing due to the Coulomb correlations, neglected within the Hartree-Fock approximation. In Ref. 8, it was shown that the Boltzmann picture of relaxation is inadequate for extremely short optical pulse durations. In Ref. 9, it was observed that the time decay and spectral width of the four-wave mixing polarization did not correlate with the decay of the time-integrated signal, as would have been expected based on the SBE's. Experimental evidence for the effects of the bound biexciton state (not described by the SBE's) was presented, e.g., in Ref. 10. Correlation effects due to the repulsive exciton-exciton interaction were found to significantly enhance the four-wave-mixing signal for negative time delays as function of magnetic field, even in the absence of bound biexciton states.<sup>11</sup> Excitation-induced dephasing effects were observed, e.g., in Ref. 12.

Experiments such as those mentioned above point out the need to incorporate in the theory exciton-exciton correlations beyond the time-dependent Hartree-Fock approximation. This problem has been addressed within the equations-of-motion approach for density matrices, which, to a given order in the optical fields, leads to a closed system of differential equations that determine the nonlinear polarizations.<sup>6,13,14</sup> The solution of such equations, however, must address the formidable four-body problem of two electrons interacting with two holes. With the exception of one-dimensional systems<sup>14</sup>, the determination of such biexciton states is numerically very demanding. Various approximation schemes, devised mainly for calculations of the third-order polarization,  $\chi^{(3)}$ , have been recently proposed.<sup>6,13,14</sup> The  $e$ - $h$  Coulomb correlations also strongly affect the *coherent* polarization femtosecond dynamics in doped quantum wells.<sup>15,16</sup> Such effects originate from the dynamical Fermi sea response to the photoexcited valence holes,<sup>1,2</sup> and can be observed for frequencies close to the Fermi energy, where the absorption spectrum is dominated by the Fermi-edge singularity and the

$e$ - $e$  quasiparticle scattering is inhibited.<sup>17,18,20</sup> The ultrafast dynamics of the Fermi-edge singularity was addressed in Ref. 16.

In this paper, we develop a new approach for describing correlation effects in ultrafast nonlinear spectroscopy. Our approach is motivated by the fact that the nonlinear polarization measured in pump-probe or four-wave-mixing experiments arises from the linear response to the probe optical field (propagating along direction  $\mathbf{k}_\tau$ ) of a system described by the Hamiltonian  $H + H_p(t)$ , where  $H$  is the two-band interacting Hamiltonian in the absence of optical fields and  $H_p(t)$  describes the coupling to the pump optical field (propagating along direction  $\mathbf{k}_p$ ). Terms nonlinear in the probe optical field do not contribute to the third-order polarizations measured along directions  $\mathbf{k}_\tau$  (pump-probe) or  $2\mathbf{k}_p - \mathbf{k}_\tau$  (wave-mixing). They can also be neglected when the probe is weaker than the pump field, as is often the case experimentally. However, unlike the “bare” Hamiltonians  $H$ , the Hamiltonian  $H + H_p(t)$  does not conserve the number of  $e$ - $h$  pairs. The idea is to “block-diagonalize” the Hamiltonian  $H + H_p(t)$  in the basis of states with fixed number of  $e$ - $h$  excitations, such as, e.g., exciton states, biexciton states etc. This can be achieved to any given order in the optical fields by using Van Vleck canonical transformations,<sup>21,22</sup> generalized to the time-dependent case. This way we obtain an effective *time-dependent* Hamiltonian,  $H_{\text{eff}}(t)$  which, *does* conserve the number of  $e$ - $h$  excitations. Note that for the time-independent case, such a procedure is analogous to the Schrieffer-Wolff transformation used to eliminate the charge fluctuations in the Anderson Hamiltonian,<sup>23,24</sup> where  $H_{\text{eff}}$  corresponds to the Kondo Hamiltonian.

The above procedure allows us to cast the experimentally-measurable nonlinear polarizations in the form of the linear polarization of an effective two-band system. The latter is characterized by time-dependent band dispersion relations, interaction potentials, and transition matrix elements, which can be obtained to any given order in the pump optical field. In particular, as we will show, to second order in the pump field the above effective parameters can be expressed in terms of the one- and two-exciton Green functions for the “bare” Hamiltonian  $H$ . Such a formulation allows us to interpret the various dynamical features in the nonlinear absorption spectra, originating from the correlation effects, within the familiar framework developed for linear spectroscopy.

In particular, in linear absorption, the strength and spectral position of the excitonic resonances are determined by (i) the dipole transition matrix elements and (ii) the time evolution of the  $e$ - $h$  pair wavefunction. Here we establish a similar picture for the nonlinear absorption spectrum, which applies for any pulse duration: (i) The  $e$ - $h$  pair photoexcited by the probe interacts with the  $e$ - $h$  pairs photoexcited by the pump via the Pauli principle (Phase Space Filling effect), static exciton-exciton interactions (Hartree-Fock contribution), and exciton-exciton scattering processes that involve the exchange of center-of-mass momentum (correlation effects). Such effects are described by a renormalized transition matrix element. (ii) Similar interactions also lead to a pump-induced renormalization of the semiconductor band energies and  $e$ - $h$  interaction potential, which affect the time evolution of the (probe-induced)  $e$ - $h$  pair wavefunction. The corresponding time evolution operator that creates the excitonic resonance is governed by the Hermitean effective Hamiltonian  $H_{\text{eff}}(t)$  which, importantly, has the same form as  $H$ . Therefore, the nonlinear absorption spectrum can be viewed as arising from the probe-induced optical transitions to renormalized (“dressed”) exciton states, which are determined by the Schrödinger equation with Hamiltonian  $H_{\text{eff}}(t)$ . One, thus, should distinguish between two physically-distinct origins of the

optical nonlinearity: optically-induced renormalizations of the transition matrix elements and time-dependent parameter renormalizations in the Hamiltonian. The latter not only shift the bound state energy, as would have been the case within the two-level system approximation, but also changes its wavefunction and Bohr radius that determine the exciton oscillator strength. Importantly, due to the Coulomb interactions,  $H_{\text{eff}}(t)$  does not commute with itself at different times (unlike for monochromatic photoexcitation), which leads to quantum dynamics and memory effects that, as we show, are not captured by the third-order nonlinear response ( $\chi^{(3)}$ ) or by using few-level system truncations. Here we provide a systematic method for including all the above effects in a physically-intuitive fashion.

The paper is organized as follows. In Section II we set up the problem and briefly outline our final results. In Section III we describe the canonical transformations that eliminate all optically-induced charge fluctuations up to the second order in the pump field. In Section IV we obtain the linear response of the system to the probe optical field. In Section V we focus on the pump-probe nonlinear polarization and identify the effective Hamiltonian and optical transition operator. In Section VI we derive the four-wave-mixing polarization. Section VII concludes the paper.

## II. PROBLEM SET-UP

In the absence of optical fields, the excitation spectrum of a two-band semiconductor is described by the Hamiltonian

$$H = \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}}^v b_{-\mathbf{q}}^\dagger b_{-\mathbf{q}} + \sum_{\mathbf{q}} (\varepsilon_{\mathbf{q}}^c + E_g) a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + V_{ee} + V_{hh} + V_{eh}, \quad (1)$$

where  $a_{\mathbf{q}}^\dagger$  is the creation operator of a conduction electron with energy  $\varepsilon_{\mathbf{q}}^c$  and mass  $m_e$ ,  $b_{-\mathbf{q}}^\dagger$  is the creation operator of a valence hole with energy  $\varepsilon_{\mathbf{q}}^v$  and mass  $m_h$ ,  $V_{ee}$ ,  $V_{eh}$ , and  $V_{hh}$  describe the  $e$ - $e$ ,  $e$ - $h$ , and  $h$ - $h$  interactions, respectively, and  $E_g$  is the bandgap. For simplicity, we consider a single parabolic valence band and suppress the spin degrees of freedom.

Ultrafast pump-probe and wave-mixing spectroscopy measures the response of such a system to photoexcitation by a pump optical field,  $E_p(t)e^{i\mathbf{k}_p \cdot \mathbf{r} - i\omega_p t}$  (with  $E_p(t)$  centered at  $t = 0$ ), and a probe optical field,  $E_\tau(t)e^{i\mathbf{k}_\tau \cdot \mathbf{r} - i\omega_p(t-\tau)}$  (with  $E_\tau(t)$  centered at  $t = \tau$ ), propagating along directions  $\mathbf{k}_p$  and  $\mathbf{k}_\tau$ , respectively, and have central frequency  $\omega_p$  and time-delay  $\tau$ . In the rotating wave approximation,<sup>25</sup> the coupling to the optical field is described by the Hamiltonian  $H_p(t)$  (pump),

$$H_p(t) = d_p(t) \left[ e^{i\mathbf{k}_p \cdot \mathbf{r}} U^\dagger + H.c. \right], \quad (2)$$

and the Hamiltonian  $H_\tau(t)$  (probe),

$$H_\tau(t) = d_\tau(t) \left[ e^{i\mathbf{k}_\tau \cdot \mathbf{r} + i\omega_p \tau} U^\dagger + H.c. \right], \quad (3)$$

where  $U^\dagger = \sum_{\mathbf{q}} a_{\mathbf{q}}^\dagger b_{-\mathbf{q}}^\dagger$  is the “bare” optical transition operator,  $d_i(t) = \mu E_i(t)$ ,  $i = p, \tau$  are the dipole energies, and  $\mu$  is the interband transition matrix element. The total Hamiltonian, including the coupling to the optical fields, is

$$H_{\text{tot}}(t) = H + H_p(t) + H_\tau(t) - \hbar\omega_p \sum_{\mathbf{q}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}}. \quad (4)$$

In the following, we will absorb the last term into  $H$ .

The pump-probe and four-wave-mixing signals are determined by the polarization

$$P(t) = \mu e^{-i\omega_p t} \langle \Psi(t) | U | \Psi(t) \rangle, \quad (5)$$

where the state  $|\Psi(t)\rangle$  satisfies the time-dependent Schrödinger equation with the Hamiltonian  $H_{\text{tot}}(t)$ . In the following, we distinguish between pump and probe optical fields by concentrating on the polarizations that propagate along direction  $\mathbf{k}_\tau$  (pump-probe) and  $2\mathbf{k}_p - \mathbf{k}_\tau$  (four-wave-mixing). For a weak probe, the nonlinear polarizations arise from the linear response to the probe-induced perturbation  $H_\tau(t)$  of the coupled-two-band system described by the time-dependent Hamiltonian  $H + H_p(t)$ . Note that, for  $\chi^{(3)}$  along the above directions, the above is also true even if the probe and pump fields have comparable strength. In contrast to  $H$ , this Hamiltonian does not conserve the number of  $e$ - $h$  pairs, so we transform it into an effective Hamiltonian  $H_{\text{eff}}(t)$  that has this property by using canonical (Van-Vleck) transformations.<sup>21–23</sup>

Specifically, the Hilbert space of the bare semiconductor states (in the absence of optical fields) consists of disconnected subspaces, which can be labelled by the number of  $e$ - $h$  pairs. In this basis,  $H$  has block-diagonal form. The Hamiltonian  $H_p(t)$  couples the different subspaces by creating/annihilating  $e$ - $h$  pairs. A unitary transformation that “block-diagonalizes” the Hamiltonian  $H + H_p(t)$ , e.g., up to the second order in pump field, has the form  $e^{-S_2} e^{-S_1} [H + H_p(t)] e^{S_1} e^{S_2}$ , where the antihermitian operators  $S_1(t)$  and  $S_2(t)$  create/annihilate one and two  $e$ - $h$  pairs, respectively. In order to achieve this in higher orders in the pump field, we should also include in  $S_1(t)$  and  $S_2(t)$  processes that create/annihilate odd and even numbers of  $e$ - $h$  pairs, respectively. Correspondingly, the state  $|\Psi(t)\rangle$  is given by

$$|\Psi(t)\rangle = e^{S_1(t)} e^{S_2(t)} |\Phi(t)\rangle \quad (6)$$

where all the effects of the probe optical field are contained in the state  $|\Phi(t)\rangle$ . After the transformation operators  $S_i^{(n)}(t)$  are calculated and the effective Hamiltonian  $H_{\text{eff}}(t)$  is derived, the polarization Eq. (5) with  $|\Psi(t)\rangle$  given by Eq. (6) can be found in the first order in the probe field by identifying all contributions that propagate along directions  $\mathbf{k}_\tau$  (pump-probe) or  $2\mathbf{k}_p - \mathbf{k}_\tau$  (four-wave-mixing).

Let us summarize our results for undoped semiconductors. The pump-probe nonlinear polarization,  $P_{\mathbf{k}_\tau}$  can be presented as a sum of two terms,  $P_{\mathbf{k}_\tau}(t) = P_{\mathbf{k}_\tau}^{(\text{exc})}(t) + P_{\mathbf{k}_\tau}^{(\text{biexc})}(t)$ , where  $P_{\mathbf{k}_\tau}^{(\text{exc})}(t)$  and  $P_{\mathbf{k}_\tau}^{(\text{biexc})}(t)$  are polarizations due to the transitions from the full valence band ground state to exciton and biexciton states, respectively. In particular,

$$P_{\mathbf{k}_\tau}^{(\text{exc})}(t) = -\frac{i}{\hbar} e^{i\mathbf{k}_\tau \cdot \mathbf{r} - i\omega_p(t-\tau)} \int_{-\infty}^t dt' d_\tau(t') \langle 0 | U_{\text{exc}}(t) \mathcal{U}(t, t') U_{\text{exc}}^\dagger(t') | 0 \rangle, \quad (7)$$

where

$$U_{\text{exc}}^\dagger(t) | 0 \rangle = \sum_{\mathbf{k}} M_{\mathbf{k}}(t) a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger | 0 \rangle \quad (8)$$

is the effective optical transition operator to exciton states,  $M_{\mathbf{k}}(t)$  being the corresponding matrix element. Here  $\mathcal{U}(t, t')$  is the time-evolution operator satisfying the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \mathcal{U}(t, t') = H_{\text{eff}}(t) \mathcal{U}(t, t'), \quad (9)$$

where  $H_{\text{eff}}(t)$  is the effective semiconductor Hamiltonian that acts on the single  $e$ - $h$  pair subspace. We show that  $H_{\text{eff}}(t)$  can be cast in the same form as  $H$ :

$$H_{\text{eff}}(t) = \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}}^c(t) a_{\mathbf{q}}^{\dagger} a_{\mathbf{q}} + \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}}^v(t) b_{-\mathbf{q}}^{\dagger} b_{-\mathbf{q}} - \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} v_{eh}(\mathbf{k}, \mathbf{k}'; t) a_{\mathbf{k}}^{\dagger} b_{-\mathbf{k}}^{\dagger} b_{-\mathbf{k}'} a_{\mathbf{k}'}. \quad (10)$$

Explicit expressions for the renormalized matrix elements and parameters of  $H_{\text{eff}}(t)$  in terms of the single- and two-exciton correlation functions are derived in Section V. The biexcitonic contribution to the pump-probe nonlinear polarization is given by an expression similar to Eq. (7), with the corresponding two-pair transition operator  $U_{\text{biexc}}^{\dagger}(t)$  (see Section V).

Note that in the absence of pump-induced photoexcitations,  $E_p(t) = 0$ , the familiar form of the linear absorption spectrum<sup>24</sup> is simply recovered from Eq. (7) by setting  $\mathcal{U}(t, t') \rightarrow e^{-\frac{i}{\hbar} H(t-t')}$  and  $U_{\text{exc}}^{\dagger}(t) \rightarrow U^{\dagger}$ . The similar second-quantized forms of Hamiltonians  $H_{\text{eff}}(t)$  and  $H$  suggest an interpretation of the excitonic effects in the nonlinear absorption spectrum in terms of probe-induced optical transitions to “dressed” exciton states. This analogy becomes more clear if one expresses the time-evolution operator  $\mathcal{U}(t, t')$  in the basis of states  $|\Phi_n^{(1)}(t)\rangle$ ,

$$\mathcal{U}(t, t') = \sum_n |\Phi_n^{(1)}(t)\rangle \langle \Phi_n^{(1)}(t')|, \quad (11)$$

which satisfy the Schrödinger equation for the Hermitean Hamiltonian  $H_{\text{eff}}(t)$  with the initial condition that, before the pump pulse,  $|\Phi_n^{(1)}(t)\rangle$  coincide with the exciton eigenstates of  $H$ .

As we will show in the next Section, the time-dependence of the parameters in the effective Hamiltonian Eq. (10) follows that of the pump amplitude. Therefore, as can be seen from Eq. (9), one can replace  $\mathcal{U}(t, t')$  by  $e^{-iH(t-t')/\hbar}$  when the probe comes at time  $t' = \tau$  *after* the pump. Thus the optically-induced corrections in  $H_{\text{eff}}(t)$  affect the pump-probe spectra only for negative probe delays or when the two pulses overlap in time. Furthermore, their effects are most pronounced in pump-probe spectroscopy, where, unlike in four-wave-mixing, they already contribute to the third-order nonlinear polarization. On the other hand, the optically-induced renormalization in the matrix element  $M_{\mathbf{k}}(t)$ , which includes contributions from the Phase Space Filling as well as from the exciton-exciton interactions (see Section V), is finite even after the pump optical field is gone and therefore dominates the pump-probe signal for positive probe delays. The same is true for the biexcitonic contribution to the pump-probe nonlinear polarization, which, as discussed below, vanishes for negative time delays.

### III. PHOTOEXCITATION BY THE PUMP OPTICAL FIELD

### A. Elimination of single-pair transitions

Our goal is to “block-diagonalize” the Hamiltonian  $H + H_p(t)$  by performing the canonical transformation Eq. (6). In this subsection we determine the transformation operator  $S_1(t)$  that eliminates the single-pair pump-induced transitions. We start with a slightly more general problem, useful for calculating higher order nonlinear polarizations, by deriving a differential equation for the operator  $S(t)$  which ensures that all *odd*-pair charge fluctuations are eliminated from the transformed Hamiltonian.<sup>21</sup>

In the time-dependent Schrödinger equation  $[i\hbar\partial/\partial t - H_{tot}(t)]|\Psi(t)\rangle = 0$  we substitute  $|\Psi(t)\rangle = e^{S(t)}|\chi(t)\rangle$  and, after acting with the operator  $e^{-S(t)}$  on its lhs, we get

$$e^{-S(t)} \left[ i\hbar \frac{\partial}{\partial t} - H \right] e^{S(t)} |\chi(t)\rangle = e^{-S(t)} [H_p(t) + H_\tau(t)] e^{S(t)} |\chi(t)\rangle. \quad (12)$$

Since both  $S(t)$  and  $H_p(t)$  create/annihilate odd numbers of  $e$ - $h$  pairs and  $H$  conserves the number of  $e$ - $h$  pairs, all odd-pair contributions to  $|\chi(t)\rangle$  originate from terms in the Taylor expansion of the exponentials in Eq. (12) of the order of  $(S)^{2n+1} (i\hbar \frac{\partial}{\partial t} - H)$  or  $(S)^{2n} H_p$ ,  $n$  being an integer. Following Ref. 22, we determine  $S(t)$  by requiring that all such terms, which describe pump-induced charge fluctuations, cancel out.

Using the Baker-Campbell-Hausdorff expansion for an arbitrary operator  $A(t)$ ,

$$e^{-S(t)} A(t) e^{S(t)} = [\cosh \hat{S}(t) + \sinh \hat{S}(t)] A(t), \quad (13)$$

where  $\hat{S}(t)$  is a superoperator defined by  $\hat{S}(t)A(t) = [A(t), S(t)]$ , we find that  $S(t)$  should satisfy

$$i\hbar \sinh[\hat{S}(t)] \frac{\partial}{\partial t} = \sinh[\hat{S}(t)] H + \cosh[\hat{S}(t)] H_p(t). \quad (14)$$

Such a form is inconvenient, however, since the lhs includes multiple commutators of  $S(t)$  with its time-derivatives. These can be eliminated by applying  $\hat{S}(t) \sinh^{-1} \hat{S}(t)$  (defined by its Taylor expansion) to both sides of Eq. (14). Using the relation  $\hat{S} \frac{\partial S}{\partial t} = \frac{\partial S}{\partial t}$ , we obtain

$$i\hbar \frac{\partial S(t)}{\partial t} = [H, S(t)] + \hat{S}(t) \coth[\hat{S}(t)] H_p(t), \quad (15)$$

with the initial condition  $S(-\infty) = 0$ .

Eliminating all contributions to Eq. (12) with odd numbers of  $e$ - $h$  pairs by using Eq. (15), we obtain after collecting the remaining terms

$$\cosh[\hat{S}(t)] \left[ i\hbar \frac{\partial}{\partial t} - H \right] |\chi(t)\rangle = \sinh[\hat{S}(t)] H_p(t) |\chi(t)\rangle + e^{-S(t)} H_\tau(t) e^{S(t)} |\chi(t)\rangle. \quad (16)$$

This equation, however, is not particularly useful because it does not have the form of a Schrödinger equation. After some manipulations involving adding and subtracting the operator  $i\hbar \frac{\partial}{\partial t} - H$  and inserting the identity  $(\hat{S})^{-1} \hat{S} = 1$ , it can be rewritten in the form

$$\begin{aligned} \left(i\hbar \frac{\partial}{\partial t} - H\right) |\chi(t)\rangle = & - [\cosh[\hat{S}(t)] - 1] [\hat{S}(t)]^{-1} \hat{S}(t) \left(i\hbar \frac{\partial}{\partial t} - H\right) |\chi(t)\rangle \\ & + \sinh[\hat{S}(t)] H_p(t) |\chi(t)\rangle + e^{-S(t)} H_\tau(t) e^{S(t)} |\chi(t)\rangle. \end{aligned} \quad (17)$$

We now simplify the first term on the rhs of Eq. (17) by making use of Eq. (15). After some algebra, we finally obtain

$$i\hbar \frac{\partial |\chi(t)\rangle}{\partial t} = \left[ H + \tanh \left[ \frac{\hat{S}(t)}{2} \right] H_p(t) \right] |\chi(t)\rangle + e^{-S(t)} H_\tau(t) e^{S(t)} |\chi(t)\rangle. \quad (18)$$

Eq. (18) now has the form of the Schrödinger equation for  $|\chi(t)\rangle$ , with a time-dependent Hamiltonian depending on  $S(t)$ . The above derivation generalizes the results of Ref. 22 to time-dependent systems.

The operator  $S_1$ , which eliminates the single-pair excitations, can be obtained by linearizing Eq. (15). The nonlinear in  $S_1$  terms in Eqs. (15) and (18) describe the corrections in the effective semiconductor parameters of the order of  $E_p^4$  or higher. Using the decomposition of the anti-hermitian operator  $S_1(t)$ ,

$$S_1(t) = \Sigma_1(t) e^{-i\mathbf{k}_p \cdot \mathbf{r}} - \Sigma_1^\dagger(t) e^{i\mathbf{k}_p \cdot \mathbf{r}}, \quad (19)$$

where  $\Sigma_1^\dagger(t)$  and  $\Sigma_1(t)$  create and annihilate single  $e$ - $h$  pairs, respectively, we obtain the following equation for  $\Sigma_1^\dagger(t)$ :

$$i\hbar \frac{\partial \Sigma_1^\dagger(t)}{\partial t} = [H, \Sigma_1^\dagger(t)] - d_p(t) U^\dagger, \quad (20)$$

which has the formal solution

$$\Sigma_1^\dagger(t) = \frac{i}{\hbar} \int_{-\infty}^t dt' d_p(t') e^{iH(t'-t)/\hbar} U^\dagger e^{-iH(t'-t)/\hbar}. \quad (21)$$

Note that, since the Hamiltonian  $H$  conserves the number of  $e$ - $h$  pairs and the optical transition operator  $U^\dagger$  creates a single  $e$ - $h$  pair,  $\Sigma_1^\dagger(t)$  also creates a single  $e$ - $h$  pair. Furthermore, since both  $H$  and  $U^\dagger$  conserve momentum, so does  $\Sigma_1^\dagger(t)$ .

It is convenient to represent  $\Sigma_1^\dagger(t)$  as a sum of one-body and many-body parts,

$$\Sigma_1^\dagger(t) = \Sigma_x^\dagger(t) + \Sigma_{xx}^\dagger(t), \quad (22)$$

where

$$\Sigma_x^\dagger(t) = \sum_{\mathbf{q}} P_x(\mathbf{q}, t) a_{\mathbf{q}}^\dagger b_{-\mathbf{q}}^\dagger \quad (23)$$

describes the photoexcitation of a single  $e$ - $h$  pair (or exciton) with zero total momentum, while the many-body operator  $\Sigma_{xx}^\dagger(t)$  contains quartic and higher order terms in the single-particle operators. As we discuss later, in undoped semiconductors,  $\Sigma_{xx}^\dagger(t)$  describes the exciton-exciton interactions. After substituting Eq. (22) into Eq. (20) and collecting all terms quadratic in the single particle operators, we obtain



$$i\hbar \frac{\partial}{\partial t} P_x(\mathbf{q}, t) = (\Delta\Omega + \varepsilon_{\mathbf{q}}^c + \varepsilon_{\mathbf{q}}^v) P_x(\mathbf{q}, t) - \sum_{\mathbf{q}'} v(\mathbf{q} - \mathbf{q}') P_x(\mathbf{q}', t) - d_p(t), \quad (24)$$

where  $v(\mathbf{q})$  is the Coulomb potential and  $\Delta\Omega = E_g - \hbar\omega_p$  is the detuning. Thus, the amplitude  $P_x(\mathbf{q}, t)$  is just the linear polarization due to the pump field. This can also be seen by substituting Eq. (6) into the polarization equation Eq. (5) (with  $S_p^{(2)} = 0$ ) in the absence of the probe field.

Note that, due to the interaction terms in  $H$ , the commutator in the rhs of Eq. (20) generates the following terms, quartic in the single-particle operators:

$$U_{xx}^\dagger(t) = \sum_{\mathbf{k}\mathbf{q}} v(\mathbf{q}) [P_x(\mathbf{k}, t) - P_x(\mathbf{k} - \mathbf{q}, t)] U_{xx}^\dagger(\mathbf{k}, \mathbf{q}), \quad (25)$$

with

$$U_{xx}^\dagger(k, \mathbf{q}) = \sum_{\mathbf{k}'} \left( a_{\mathbf{k}-\mathbf{q}}^\dagger b_{-\mathbf{k}}^\dagger a_{\mathbf{k}'+\mathbf{q}}^\dagger a_{\mathbf{k}'} - a_{\mathbf{k}-\mathbf{q}}^\dagger b_{-\mathbf{k}}^\dagger b_{-\mathbf{k}'+\mathbf{q}}^\dagger b_{-\mathbf{k}'} \right). \quad (26)$$

Thus, we get the following equation for  $\Sigma_{xx}^\dagger(t)$ :

$$i\hbar \frac{\partial \Sigma_{xx}^\dagger(t)}{\partial t} = [H, \Sigma_{xx}^\dagger(t)] + U_{xx}^\dagger(t), \quad (27)$$

which has the formal solution

$$\Sigma_{xx}^\dagger(t) = \frac{i}{\hbar} \sum_{\mathbf{k}\mathbf{q}} v(\mathbf{q}) \int_{-\infty}^t dt' [P_x(\mathbf{k} - \mathbf{q}, t') - P_x(\mathbf{k}, t')] U_{xx}^\dagger(\mathbf{k}, \mathbf{q}, t - t'), \quad (28)$$

with

$$U_{xx}^\dagger(\mathbf{k}, \mathbf{q}, t) = e^{-iHt/\hbar} U_{xx}^\dagger(\mathbf{k}, \mathbf{q}) e^{iHt/\hbar}. \quad (29)$$

As can be seen from Eq. (28),  $\Sigma_{xx}^\dagger(t)$  describes the photoexcitation of a single  $e$ - $h$  pair accompanied by Coulomb interactions with additional photoexcited or Fermi sea carriers. Note that the time evolution of  $\Sigma_{xx}^\dagger(t)$  is driven by the linear pump-induced *polarization* and thus, in contrast to  $\Sigma_x^\dagger(t)$ , only indirectly depends on the pump amplitude  $d_p(t)$ .

We now turn to the Schrödinger equation Eq. (18). The leading-order corrections to the effective Hamiltonian are given by the terms linear in  $S_1$ . With the help of Eq. (19) we obtain

$$\left[ i\hbar \frac{\partial}{\partial t} - H_{\text{eff}}(t) \right] |\chi(t)\rangle = -\frac{d_p(t)}{2} \left( e^{2i\mathbf{k}_p \mathbf{r}} [U^\dagger, \Sigma_1^\dagger(t)] + H.c. \right) |\chi(t)\rangle + e^{-S_1(t)} H_\tau(t) e^{S_1(t)} |\chi(t)\rangle. \quad (30)$$

where

$$H_{\text{eff}}(t) = H - \frac{d_p(t)}{2} ([U, \Sigma_1^\dagger(t)] + H.c.) \quad (31)$$

is a time-dependent effective Hamiltonian that conserves the number of  $e$ - $h$  pairs and  $\Sigma_1^\dagger(t)$  is given by Eq. (20) with initial condition  $\Sigma_1^\dagger(-\infty) = 0$ . The first term in the rhs of

Eq. (30) describes the pump-induced two-pair creation/annihilation processes. These can be eliminated by performing a second canonical transformation, as described in the next subsection.

Concluding this subsection, let us address the condition of validity of our approach. It is useful to write down a formal solution of Eq. (20) in the basis of the  $N$ -hole many-body eigenstates,  $|\alpha N\rangle$  with energies  $E_{\alpha N}$ , of the Hamiltonian  $H$ . Here, for example,  $N=0$  gives the semiconductor ground state  $|0\rangle$ ,  $|\alpha 1\rangle$  denotes the exciton eigenstates,  $|\alpha 2\rangle$  denotes the biexciton eigenstates, etc. In this basis, the solution of Eq. (20) can be written as

$$\frac{\langle \beta N + 1 | \Sigma_1^\dagger(t) | \alpha N \rangle}{\langle \beta N + 1 | U^\dagger | \alpha N \rangle} = \frac{i}{\hbar} \int_{-\infty}^t d_p(t') e^{\frac{i}{\hbar}(t'-t)(\Delta\Omega + \Delta E_{\alpha\beta}^N)} e^{-\Gamma(t-t')} dt', \quad (32)$$

where we separated out the detuning  $\Delta\Omega$  and denoted  $\Delta E_{\alpha\beta}^N = E_{\beta N+1} - E_{\alpha N}$ ; the width  $\Gamma$  describes the effects of dephasing processes not included in  $H$  (e.g., due to phonons). It can be seen that for resonant excitations (small  $\Delta\Omega$ ) the rhs is of the order of  $d_p t_p / \hbar$ . Thus, for short pulses, this parameter justifies the expansion in terms of optical fields. Note that, for off-resonant excitation, this expansion is valid even for longer pulse durations.

## B. Elimination of two-pair transitions

We now perform the second canonical transformation in order to eliminate the first term in the rhs of Eq. (30), which describes biexcitonic transitions. We define

$$|\chi(t)\rangle = e^{S_2(t)} |\Phi(t)\rangle, \quad (33)$$

where, in the absence of the probe field,  $|\Phi(t)\rangle$  has fixed number of  $e$ - $h$  pairs. Again, using the anti-Hermiticity of  $S_2(t)$ , we decompose it as

$$S_2(t) = \Sigma_2(t) e^{-2i\mathbf{k}_p \cdot \mathbf{r}} - \Sigma_2^\dagger(t) e^{2i\mathbf{k}_p \cdot \mathbf{r}}, \quad (34)$$

where  $\Sigma_2^\dagger(t)$  and  $\Sigma_2(t)$  create and annihilate two  $e$ - $h$  pairs, respectively. Substituting Eq. (33) into Eq. (30) and requiring that all two-pair terms cancel out, we obtain similar to the previous subsection the following equation for  $\Sigma_2^\dagger(t)$  to the leading order,

$$i\hbar \frac{\partial \Sigma_2^\dagger(t)}{\partial t} = [H, \Sigma_2^\dagger(t)] - \frac{d_p(t)}{2} [\Sigma_1^\dagger(t), U^\dagger], \quad (35)$$

which has the solution

$$\Sigma_2^\dagger(t) = \frac{i}{2\hbar} \int_{-\infty}^t dt' d_p(t') e^{iH(t'-t)/\hbar} [\Sigma_1^\dagger(t'), U^\dagger] e^{-iH(t'-t)/\hbar}. \quad (36)$$

As we will show later,  $\Sigma_2^\dagger(t)$  includes all exciton-exciton interaction contributions to the third-order four-wave-mixing polarization but only affects the pump-probe signal via higher order ( $E_p^4$ ) parameter renormalizations.

## IV. PROBE-INDUCED OPTICAL TRANSITIONS

In the previous section, we “block-diagonalized” the Hamiltonian  $H + H_p(t)$  (up to the second order in the pump field) in the basis of states which, in the absence of the probe optical field, conserve the number of  $e$ - $h$  pairs. In the presence of the probe field, the state  $|\Phi(t)\rangle$  (Eq. (33)) satisfies the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Phi(t)\rangle = H_{\text{eff}}(t) |\Phi(t)\rangle + d_\tau(t) \left[ e^{i\mathbf{k}_\tau \mathbf{r} + i\omega_p \tau} U_r^\dagger(t) + H.c. \right] |\Phi(t)\rangle, \quad (37)$$

where  $H_{\text{eff}}(t)$  is given by Eq. (31) and

$$U_r^\dagger(t) = e^{-S_2(t)} e^{-S_1(t)} U^\dagger e^{S_1(t)} e^{S_2(t)} \quad (38)$$

is the (transformed) optical transition operator. Following the standard procedure, we obtain in the first order in the probe field

$$|\Phi(t)\rangle = \left\{ 1 - \frac{i}{\hbar} \int_{-\infty}^t d_\tau(t') \mathcal{U}(t, t') \left[ e^{i\mathbf{k}_\tau \mathbf{r} + i\omega_p \tau} U_r^\dagger(t') + H.c. \right] \right\} |\Phi^{(0)}(t')\rangle, \quad (39)$$

where  $\mathcal{U}(t, t')$  is the time-evolution operator satisfying

$$i\hbar \frac{\partial}{\partial t} \mathcal{U}(t, t') = H_{\text{eff}}(t) \mathcal{U}(t, t'), \quad (40)$$

and  $|\Phi^{(0)}(t)\rangle = \mathcal{U}(t, -\infty)|0\rangle$  is the time-evolved ground state  $|0\rangle$ . Since  $H_{\text{eff}}(t)$  conserves the number of  $e$ - $h$  pairs,  $|\Phi^{(0)}(t)\rangle$  contains no  $e$ - $h$  pairs. In undoped semiconductors, the only such state is the ground state so that  $|\Phi^{(0)}(t)\rangle \propto |0\rangle$ .

Using Eq. (39) for  $|\Phi(t)\rangle$ , the polarization  $P(t) = \mu e^{-i\omega_p t} \langle \Psi(t) | U | \Psi(t) \rangle = \mu e^{-i\omega_p t} \langle \Phi(t) | U_r(t) | \Phi(t) \rangle$  can be written as

$$\begin{aligned} P(t) = & -\frac{i\mu}{\hbar} e^{-i\omega_p t} \int_{-\infty}^t d_\tau(t') \\ & \times \{ \langle 0 | U_r(t) \mathcal{U}(t, t') [e^{i\mathbf{k}_\tau \mathbf{r} + i\omega_p \tau} U_r^\dagger(t') + e^{-i\mathbf{k}_\tau \mathbf{r} - i\omega_p \tau} U_r(t')] | 0 \rangle \\ & - \langle 0 | [e^{i\mathbf{k}_\tau \mathbf{r} + i\omega_p \tau} U_r^\dagger(t') + e^{-i\mathbf{k}_\tau \mathbf{r} - i\omega_p \tau} U_r(t')] \mathcal{U}(t', t) U_r(t) | 0 \rangle \}. \end{aligned} \quad (41)$$

Explicit expressions for  $U_r^\dagger(t)$  are derived in the next sections.

## V. PUMP-PROBE SPECTRUM

### A. Pump-probe polarization

In this section we derive the closed form expression for the nonlinear polarization propagating in the direction of the probe optical field. In order to extract the pump-probe polarization from Eq. (41), one should retain only contributions that are proportional to  $e^{i\mathbf{k}_\tau \mathbf{r}}$  and are independent of the pump direction  $\mathbf{k}_p$ . To the leading order, the transition operator  $U_r^\dagger(t)$  can be obtained by expanding Eq. (38) in terms of  $S_1$  and  $S_2$  (given by Eqs. (19) and (34)) using the Baker–Campbell–Hausdorff formula, Eq. (13):

$$U_r^\dagger(t) = U_{\text{exc}}^\dagger(t) + e^{-i\mathbf{k}_p \mathbf{r}} U_0^\dagger(t) + U_{-1}^\dagger(t) e^{-2i\mathbf{k}_p \mathbf{r}} + U_{\text{biexc}}^\dagger(t) e^{i\mathbf{k}_p \mathbf{r}} + U_3^\dagger(t) e^{2i\mathbf{k}_p \mathbf{r}}. \quad (42)$$

(Note that the higher-order corrections do not contribute also to  $\chi^{(3)}$  measured along the probe direction.) Here the operator

$$U_{\text{exc}}^\dagger(t) = U^\dagger + \frac{1}{2} [\Sigma_1(t), [U^\dagger, \Sigma_1^\dagger(t)]] + \frac{1}{2} [\Sigma_1^\dagger(t), [U^\dagger, \Sigma_1(t)]], \quad (43)$$

creates a single  $e$ - $h$  pair; the operator

$$U_0^\dagger(t) = [U^\dagger, \Sigma_1(t)], \quad (44)$$

conserves the number of  $e$ - $h$  pairs; the operator

$$U_{\text{biexc}}^\dagger(t) = [\Sigma_1^\dagger(t), U^\dagger], \quad (45)$$

creates two  $e$ - $h$  pairs; the operator

$$U_{-1}^\dagger(t) = [U^\dagger, \Sigma_2(t)] + \frac{1}{2} [[U^\dagger, \Sigma_1(t)], \Sigma_1(t)], \quad (46)$$

annihilates a single  $e$ - $h$  pair; and the operator

$$U_3^\dagger(t) = [\Sigma_2^\dagger(t), U^\dagger] + \frac{1}{2} [[U^\dagger, \Sigma_1^\dagger(t)], \Sigma_1^\dagger(t)], \quad (47)$$

creates three  $e$ - $h$  pairs. Furthermore, it is easy to see that

$$U_r(t)|0\rangle = [e^{i\mathbf{k}_p \mathbf{r}} U_0(t) + U_{-1}(t) e^{2i\mathbf{k}_p \mathbf{r}}]|0\rangle, \quad (48)$$

and

$$U_r^\dagger(t)|0\rangle = [U_{\text{exc}}^\dagger(t) + e^{-i\mathbf{k}_p \mathbf{r}} U_0^\dagger(t) + U_{\text{biexc}}^\dagger(t) e^{i\mathbf{k}_p \mathbf{r}} + U_3^\dagger(t) e^{2i\mathbf{k}_p \mathbf{r}}]|0\rangle, \quad (49)$$

while all other terms annihilate the ground state  $|0\rangle$ . Substituting Eqs. (48) and (49) into Eq. (41) and retaining only terms proportional to  $e^{i\mathbf{k}_\tau \mathbf{r}}$ , we obtain  $P_{\mathbf{k}_\tau}(t) = P_{\mathbf{k}_\tau}^{(\text{exc})}(t) + P_{\mathbf{k}_\tau}^{(\text{biexc})}(t)$ , where

$$P_{\mathbf{k}_\tau}^{(\text{exc})}(t) = -\frac{i\mu}{\hbar} e^{i\mathbf{k}_\tau \cdot \mathbf{r} - i\omega_p(t-\tau)} \int_{-\infty}^t dt' d_\tau(t') \langle 0 | U_{\text{exc}}(t) \mathcal{U}(t, t') U_{\text{exc}}^\dagger(t') | 0 \rangle, \quad (50)$$

and

$$P_{\mathbf{k}_\tau}^{(\text{biexc})}(t) = -\frac{i\mu}{\hbar} e^{i\mathbf{k}_\tau \cdot \mathbf{r} - i\omega_p(t-\tau)} \int_{-\infty}^t dt' d_\tau(t') \langle 0 | U_{\text{biexc}}(t) \mathcal{U}(t, t') U_{\text{biexc}}^\dagger(t') | 0 \rangle. \quad (51)$$

In the derivation, all terms containing  $U_0$  cancelled each other out. Note that the above expressions apply to both undoped and doped semiconductors.

We have thus expressed the nonlinear polarizations, Eqs. (50)–(51), in terms of the linear response to the probe optical field of a system described by a Hermitean time-dependent effective Hamiltonian, Eq. (31), that does not include any charge fluctuations. The first term, Eq. (50), describes the excitonic (single-hole state) contribution to the pump-probe

polarization. Eq. (50) contributes to the pump-probe spectrum at frequencies close to the exciton energy. Since  $U_{\text{biexc}}^\dagger(t)$  creates two e-h pairs, the second term, Eq. (51), describes a biexcitonic contribution, not included in the SBE's. Note that  $\Sigma_1^\dagger(t)$ , and hence  $U_{\text{biexc}}^\dagger(t)$  vanishes if the probe pulse arrives before the pump pulse. Therefore  $P_{\mathbf{k}_\tau}^{(\text{biexc})}(t)$  is unimportant for negative time delays, for which the time-dependence of  $H_{\text{eff}}(t)$  contributes the most. Biexciton (two-hole) states also affect  $P_{\mathbf{k}_\tau}^{(\text{exc})}(t)$  by acting as intermediate states in the renormalization of the parameters entering into the optical transition operator  $U_{\text{exc}}(t)$  and the effective Hamiltonian  $H_{\text{eff}}(t)$ , as described later.

In the following sections, we focus on undoped semiconductors. We show that  $U_{\text{exc}}(t)$  and  $H_{\text{eff}}(t)$  have the same operator form as their “bare” counterparts  $U$  and  $H$ , respectively; they only differ in the parameters. This fact allows us to view the non-linear polarization as arising from the linear response to a probe-induced optical transition from the ground state to a nonstationary “dressed” exciton state evolving in time with Hamiltonian  $H_{\text{eff}}(t)$ .

## B. Optical transition matrix elements

In this subsection we derive explicit expressions for the effective transition matrix elements. We start by showing that, when acting on the ground state  $|0\rangle$ , as in Eq. (50), the operator  $U_{\text{exc}}^\dagger(t)$  has the same operator form as  $U^\dagger$ . Substituting  $\Sigma_1^\dagger(t) = \Sigma_x^\dagger(t) + \Sigma_{xx}^\dagger(t)$  into Eq. (43) and using the second-quantized expression for  $\Sigma_x^\dagger(t)$ , Eq. (23), we obtain after some algebra

$$U_{\text{exc}}^\dagger(t)|0\rangle = \sum_{\mathbf{k}} \left[1 - |P_x(\mathbf{k}, t)|^2\right] a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger |0\rangle - \frac{1}{2} \left[ \Sigma_x(t) \Sigma_{xx}^\dagger(t) - H.c. \right] U^\dagger |0\rangle - \frac{1}{2} \Sigma_{xx}(t) \Sigma_{xx}^\dagger(t) U^\dagger |0\rangle. \quad (52)$$

In deriving Eq. (52) we used the fact that  $\Sigma_1(t)$  annihilates the ground state  $|0\rangle$  and that

$$\Sigma_{xx}^\dagger(t)|0\rangle = \Sigma_{xx}(t)U^\dagger|0\rangle = \Sigma_{xx}(t)\Sigma_x^\dagger(t)|0\rangle = 0 \quad (53)$$

The latter relations can be obtained from Eqs. (28) and (26) by noting that  $H$  does not change the number of  $e$ - $h$  pairs.

It can be seen from Eqs. (52) that, since both  $\Sigma_{xx}^\dagger(t)$  and  $\Sigma_x^\dagger(t)$  create a single  $e$ - $h$  pair [see Eqs. (23), (26), and (28)], the transition operator  $U_{\text{exc}}^\dagger(t)$  also creates a single  $e$ - $h$  pair. Since, in addition, the operators  $\Sigma_{xx}^\dagger(t)$  and  $\Sigma_x^\dagger(t)$  conserve the momentum, as discussed above, we have

$$U_{\text{exc}}^\dagger(t)|0\rangle = \sum_{\mathbf{k}} M_{\mathbf{k}}(t) a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger |0\rangle. \quad (54)$$

By comparing to the “bare” transition operator,  $U^\dagger|0\rangle = \sum_{\mathbf{k}} a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger |0\rangle$ , we see that the parameter

$$M_{\mathbf{k}}(t) = \langle 0 | b_{-\mathbf{k}} a_{\mathbf{k}} U_{\text{exc}}^\dagger(t) | 0 \rangle, \quad (55)$$

should be interpreted as an effective time-dependent optical transition matrix element.

To derive an explicit expression for  $M_{\mathbf{k}}(t)$ , it is convenient to work in the exciton basis. We introduce the operators  $B_{n,\mathbf{q}}^\dagger$  and  $B_{n,\mathbf{q}}$  that create/annihilate an exciton with center-of-mass momentum  $\mathbf{q}$  and energy  $E_{n\mathbf{q}}$  in the relative motion state  $\phi_n(\mathbf{q})$ :

$$B_{n,\mathbf{q}}^\dagger = \sum_{\mathbf{k}} \phi_n(k + \beta\mathbf{q}) a_{\mathbf{k}+\mathbf{q}}^\dagger b_{-\mathbf{k}}^\dagger, \quad \beta = \frac{m_h}{m_e + m_h}, \quad (56)$$

with  $m_e$  and  $m_h$  being electron and hole mass, respectively, and define the corresponding exciton contribution to the linear polarization as

$$P_n(t) = \sum_{\mathbf{k}} P_x(\mathbf{k}, t) \phi_n^*(\mathbf{k}). \quad (57)$$

The effects of the exciton–exciton interactions can be conveniently described by introducing the correlation function

$$\Sigma_{xx}(n'm'\mathbf{q}'; n; t) = \frac{1}{2} \langle 0 | B_{n'\mathbf{q}'} B_{m'-\mathbf{q}'}^\dagger \Sigma_{xx}^\dagger(t) B_{n0}^\dagger | 0 \rangle, \quad (58)$$

which represents the contribution to the probability amplitude of pump-induced transitions between single-exciton,  $B_{n0}^\dagger | 0 \rangle$ , and two-exciton,  $B_{m'-\mathbf{q}'}^\dagger B_{n'\mathbf{q}'}^\dagger | 0 \rangle$ , states due to the exciton–exciton interactions. Such transitions also occur in the absence of interactions, with amplitude given by Eq. (58) but with  $\Sigma_{xx}^\dagger(t)$  replaced by  $\Sigma_x^\dagger(t)$ . This determines the first (Phase Space Filling) term in the rhs of Eq. (52). As we discuss below, by restricting in Eq. (58) to two-exciton states with zero center-of-mass momentum  $\mathbf{q}' = 0$ , one recovers the static exciton–exciton interaction contribution included in the SBE's.

Substituting  $a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger = \sum_n \phi_n^*(\mathbf{k}) B_{n,0}^\dagger$  into Eqs. (54) and (52) and inserting the closure relation into the last term of Eq. (52) we obtain from Eq. (54) that  $M_{\mathbf{k}}(t) = M_{\mathbf{k}}^{(\text{PSF})}(t) + M_{\mathbf{k}}^{(\text{xx})}(t)$ , where  $M_{\mathbf{k}}^{(\text{PSF})}(t) = 1 - |P_x(\mathbf{k}, t)|^2$  is the usual Phase Space Filling and  $M_{\mathbf{k}}^{(\text{xx})}(t)$  comes from the exciton–exciton interactions:

$$\begin{aligned} M_{\mathbf{k}}^{(\text{xx})}(t) = & \sum_{nn'm'} [\Phi_{n'}^* P_{m'}^*(t) \phi_n(\mathbf{k}) \Sigma_{xx}^*(n'm'0; n; t) \\ & - \Phi_n^* P_{m'}^*(t) \phi_{n'}(\mathbf{k}) \Sigma_{xx}(n'm'0; n; t)] \\ & - \frac{1}{8} \sum_{mn'm'n\mathbf{q}'} \phi_m(\mathbf{k}) \Phi_n^* \Sigma_{xx}^*(n'm'\mathbf{q}'; m; t) \Sigma_{xx}(n'm'\mathbf{q}'; n; t), \end{aligned} \quad (59)$$

where  $\Phi_n = \sum_{\mathbf{k}} \phi_n(\mathbf{k})$ . The first term in Eq. (59) contains both static exciton–exciton interactions (Hartree–Fock contribution) and exciton–exciton scattering processes (correlation contribution). It describes a process where the photoexcitation of an  $e$ – $h$  pair by the probe optical field is accompanied by the pump-induced creation and subsequent annihilation of an  $e$ – $h$  pair with zero center-of-mass momentum. Correlations contribute to this term via the process during which the pump photoexcites an  $e$ – $h$  pair with finite momentum due to scattering with the probe-induced  $e$ – $h$  pair, which then scatters back to zero momentum and subsequently annihilates. The last term in Eq. (59) describes exciton–exciton scattering processes (not included in the SBE's) where the pump photoexcites an  $e$ – $h$  pair with finite momentum due to scattering with the probe-induced  $e$ – $h$  pair, which subsequently annihilates by giving its momentum back to the probe-induced  $e$ – $h$  pair.

The contribution of the biexciton transitions,  $|0\rangle \rightarrow U_{\text{biexc}}^\dagger(t)|0\rangle$ , to the pump-probe polarization is given by Eq. (51). The biexciton optical transition operator  $U_{\text{biexc}}^\dagger(t)$ , given by Eq. (45), can be obtained in a similar manner by inserting the closure relation expressed in the basis of momentum eigenstates and noting that only two-pair states contribute. The result reads

$$U_{\text{biexc}}^\dagger(t)|0\rangle = \frac{1}{8} \sum_{n'm'q'n} \Phi_n^* \Sigma_{\text{xx}}(n'm'q'; n; t) B_{n'q'}^\dagger B_{m'-q'}^\dagger |0\rangle, \quad (60)$$

where  $\Sigma_{\text{xx}}(n'm'q'; n; t)$  is given by Eq. (58). Below we show that  $\Sigma_{\text{xx}}(n'm'q'; n; t)$  can be expressed in terms of the two-exciton Green function for the bare Hamiltonian  $H$ .

### C. Effective Hamiltonian

We now derive the second-quantized form of the effective Hamiltonian  $H_{\text{eff}}(t)$ , whose formal expression is given by Eq. (31). Here we primarily focus on the excitonic contribution to the nonlinear polarization and therefore, according to Eq. (50), we only need to consider how  $H_{\text{eff}}(t)$  acts on single-pair states. One has to distinguish between two contributions to the pump-induced correction to the Hamiltonian,  $\frac{1}{2} ([U, \Sigma_1^\dagger] + H.c.)$ , which come from the decomposition  $\Sigma_1^\dagger(t) = \Sigma_x^\dagger(t) + \Sigma_{xx}^\dagger(t)$ . The first contribution, due to the one-body single-exciton operator  $\Sigma_x^\dagger(t)$ , is also present in two-level systems. Using Eq. (23), we obtain after straightforward algebra

$$\frac{1}{2} ([U, \Sigma_x^\dagger] + H.c.) = \sum_{\mathbf{q}'} \text{Re} P_x(\mathbf{q}', t) - \sum_{\mathbf{q}'} \text{Re} P_x(\mathbf{q}', t) (a_{\mathbf{q}'}^\dagger a_{\mathbf{q}'} + b_{-\mathbf{q}'}^\dagger b_{-\mathbf{q}'}). \quad (61)$$

The second term in the rhs represents a correction to the electron and hole band energies (the first term plays no role and can be dropped). This is the origin of the energy shifts (ac-Stark effect) well-known from the dressed atom picture.<sup>22,1</sup> Here, however, the shifts are momentum-dependent. This leads, in particular, to an additional time-dependent correction to the exciton Bohr radius and wavefunction absent within the two-level system approximation.<sup>16</sup>

To derive the many-body correction to  $H_{\text{eff}}(t)$ , described by  $\Sigma_{xx}^\dagger(t)$ , we note that, according to Eqs. (50) and (54), the time evolution operator  $\mathcal{U}(t, t')$ , and hence  $H_{\text{eff}}(t)$ , only act on the state  $U_{\text{exc}}^\dagger(t)|0\rangle$  that describes a single  $e$ - $h$  pair with zero momentum. Therefore, it is sufficient to describe the action of  $H_{\text{eff}}(t)$  on the basis of states  $a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger |0\rangle$ . Since both  $\Sigma_{xx}^\dagger(t)$  and  $U^\dagger$  conserve momentum and create a single  $e$ - $h$  pair, we obtain that, when acting on states  $a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger |0\rangle$ ,

$$U \Sigma_{xx}^\dagger(t) + H.c. = \sum_{\mathbf{kp}} U_{eh}(\mathbf{p}, \mathbf{k}; t) a_{\mathbf{p}}^\dagger b_{-\mathbf{p}}^\dagger b_{-\mathbf{k}} a_{\mathbf{k}}, \quad (62)$$

where

$$U_{eh}(\mathbf{p}, \mathbf{k}, t) = \langle 0 | b_{-\mathbf{p}} a_{\mathbf{p}} [U \Sigma_{xx}^\dagger(t) + H.c.] a_{\mathbf{k}}^\dagger b_{-\mathbf{k}}^\dagger | 0 \rangle. \quad (63)$$

Following the steps described in the previous subsection and transforming to the exciton basis,  $U_{eh}(\mathbf{p}, \mathbf{k}, t)$  can be presented as

$$U_{eh}(\mathbf{p}, \mathbf{k}, t) = \sum_{nn'm'} \phi_{n'}(\mathbf{p}) \phi_n^*(\mathbf{k}) [\Phi_{m'} \Sigma_{xx}(n'm'0; n; t) + \Phi_{m'}^* \Sigma_{xx}^*(nm'0; n'; t)], \quad (64)$$

with  $\Sigma_{xx}(n'm'0; n; t)$  given by Eq. (58). Putting everything together, we finally arrive at the following second-quantized expression for  $H_{\text{eff}}(t)$ :

$$H_{\text{eff}}(t) = \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}}^c(t) a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + \sum_{\mathbf{q}} \varepsilon_{\mathbf{q}}^v(t) b_{-\mathbf{q}}^\dagger b_{-\mathbf{q}} - \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} v_{eh}(\mathbf{k}, \mathbf{k}'; t) a_{\mathbf{k}}^\dagger a_{\mathbf{k}'} b_{-\mathbf{k}}^\dagger b_{-\mathbf{k}'}, \quad (65)$$

where

$$\varepsilon_{\mathbf{q}}^i(t) = \varepsilon_{\mathbf{q}}^i + d_p(t) \text{Re} P_x(\mathbf{q}, t), \quad i = c, v, \quad (66)$$

are the time-dependent renormalized dispersion relations of electrons and holes, respectively, and

$$v_{eh}(\mathbf{k}, \mathbf{k}'; t) = v(\mathbf{k} - \mathbf{k}') - d_p(t) U_{eh}(\mathbf{k}, \mathbf{k}'; t) \quad (67)$$

is the (nonlocal) effective  $e$ - $h$  interaction.

It should be emphasized that the pump-induced parameter renormalizations in  $H_{\text{eff}}(t)$  and  $U_{\text{exc}}^\dagger(t)$  affect the polarization Eq. (50) in different ways. Indeed, the dependence of  $H_{\text{eff}}(t)$  on time follows that of the pump pulse: the last terms in Eqs. (66) and (67) are proportional to  $d_p(t)$ . Therefore, they do not affect the time-evolution operator  $\mathcal{U}(t, t')$  when the probe comes at times  $t'$  *after* the pump pulse, but do contribute to the pump-probe signal for negative probe delays or when the probe overlaps in time with the pump pulse. On the other hand, the transition operator Eq. (43) depends on the pump only via  $\Sigma_1^\dagger(t)$  and hence, according to Eq. (21), is determined by the pump amplitude at all past times  $t' \leq t$ . For positive time delays, the dynamics of the pump-probe spectra is therefore governed by the renormalized transition matrix element and the biexcitonic contribution Eq. (51). In this case, the latter is determined by the time-evolution operator corresponding to the bare Hamiltonian  $H$ .

We now discuss the role of the pump-induced corrections in the effective Hamiltonian  $H_{\text{eff}}(t)$ . As discussed in the Introduction, the spectral position and strength of the exciton resonance is determined by the time evolution operator  $\mathcal{U}(t, t')$ . In the linear response theory, this operator satisfies Eq. (40) with Hamiltonian  $H$ , while in nonlinear absorption the latter must be replaced by the effective Hamiltonian  $H_{\text{eff}}(t)$ . Therefore,  $H_{\text{eff}}(t)$  plays an important role in determining the properties of the excitonic resonance observed in the pump-probe spectrum. First, the time-dependent change in the band dispersion relations in  $H_{\text{eff}}(t)$  leads to a shift in the position of the excitonic resonance, which is, of course, the origin of the ac-Stark effect. Second, in the presence of interactions,  $H_{\text{eff}}(t)$  does not commute with itself at different times, which leads to memory effects. Importantly, such effects only arise to second or higher order in the Hamiltonian correction  $d_p(t) \Delta H(t) = -\frac{1}{2} d_p(t) ([U, \Sigma_1^\dagger] + H.c.)$  and therefore do not contribute to the third-order polarizations. To illustrate this point, let us expand  $\mathcal{U}(t, t')$  in terms of the optical field using the Magnus expansion:<sup>29</sup>

$$\mathcal{U}(t, t') = e^{-iH(t-t')/\hbar} \exp \left[ \sum_{n=1}^{\infty} \frac{1}{n!} \left( -\frac{i}{\hbar} \right)^n \mathcal{U}_n(t, t') \right], \quad (68)$$

where



$$\mathcal{U}_1(t, t') = \int_{t'}^t dt_1 d_p(t_1) e^{i \frac{H(t_1 - t')}{\hbar}} \Delta H(t_1) e^{-i \frac{H(t_1 - t')}{\hbar}}, \quad (69)$$

$$\begin{aligned} \mathcal{U}_2(t, t') &= \int_{t'}^t d_p(t_1) dt_1 \int_{t'}^{t_1} dt_2 d_p(t_2) \\ &\times \left[ e^{i \frac{H(t_1 - t')}{\hbar}} \Delta H(t_1) e^{-i \frac{H(t_1 - t')}{\hbar}}, e^{i \frac{H(t_2 - t')}{\hbar}} \Delta H(t_2) e^{-i \frac{H(t_2 - t')}{\hbar}} \right], \end{aligned} \quad (70)$$

etc. In the absence of Coulomb interactions,  $[H, \Delta H(t)] = 0$  and only the first term survives.  $\mathcal{U}_1(t, t')$  leads to the energy shifts if one does not expand the exponential. However, in order to describe the Coulomb-induced quantum dynamics emerging from the second and higher order terms in Eq. (68), one cannot restrict the pump-probe polarization to the third order in the optical fields, but rather must use the full  $\mathcal{U}(t, t')$ . Below we describe a simple physically-intuitive way, based on the similarity between  $H_{\text{eff}}(t)$  and  $H$ , for calculating the response to the probe in all orders in the optically-induced terms in  $H_{\text{eff}}(t)$ .

We start with the pump-probe polarization Eq. (50). At time  $t'$ , the probe photoexcites the system into a single-pair state  $U_{\text{exc}}^\dagger(t')|0\rangle$ , Eq. (54), with the momentum wavefunction  $M_{\mathbf{k}}(t')$ . Note that, for negative time delays,  $\Sigma_1(t') = 0$  and hence  $M_{\mathbf{k}}(t') = 1$ . The subsequent evolution of such state up to time  $t$  is governed by  $H_{\text{eff}}(t)$  and describes the formation of the exciton resonance. The momentum wavefunction of the time-evolved state,  $\Phi_{\mathbf{k}}(t)$ , satisfies the Schrödinger equation

$$i\hbar \frac{\partial \Phi_{\mathbf{k}}(t; t')}{\partial t} = [\varepsilon_{\mathbf{k}}^c(t) + \varepsilon_{\mathbf{k}}^v(t) + d_p(t)U_{\text{eh}}(\mathbf{k}, \mathbf{k}, t)] \Phi_{\mathbf{k}}(t; t') - \sum_{\mathbf{k}' \neq \mathbf{k}} v_{eh}(\mathbf{k}, \mathbf{k}', t) \Phi_{\mathbf{k}'}(t; t'), \quad (71)$$

with the initial condition  $\Phi_{\mathbf{k}}(t'; t') = M_{\mathbf{k}}(t')$ . Correspondingly, the polarization  $P_{\mathbf{k}_\tau}^{(\text{exc})}(t)$ , Eq. (50), takes the form

$$P_{\mathbf{k}_\tau}^{(\text{exc})}(t) = \int_{-\infty}^t dt' d_\tau(t') \sum_{\mathbf{k}} M_{\mathbf{k}}^*(t) \Phi_{\mathbf{k}}(t; t') \quad (72)$$

Thus, polarization dephasing arises from two different pump-induced effects: the change in the transition matrix element  $M_{\mathbf{k}}(t)$  and the time-evolution of the state  $\Phi_{\mathbf{k}}(t; t')$  due to the time-dependent coefficients in the Schrödinger equation Eq. (71). Note here that, for  $E_p(t) = 0$ ,  $M_{\mathbf{k}}(t) = 1$  and Eq. (72) reduces to the familiar Fermi's Golden Rule expression. Note also that  $M_{\mathbf{k}}(t)$  and the effective Hamiltonian parameters are time-independent in the case of monochromatic photoexcitation.

The Hamiltonian  $H_{\text{eff}}(t)$  thus determines new (“dressed”) exciton states, which depend on the time-dependent optical field amplitude and, as in the linear response theory, can be obtained by solving the Schrödinger equation Eq. (71). For example, this point of view provides a natural explanation of why, for below-resonant photoexcitation, the pump-induced coupling to higher exciton states leads to a rigid exciton blue-shift instead of bleaching, as would have been the case if only the  $1s$  bound state were included.<sup>26,4,5,27</sup> To see this, note that, to first approximation, the renormalization of the band dispersion relations, Eq. (66), results in an increase of the e-h effective mass. This in turn leads to an optically-induced decrease in the Bohr radius  $a_B$ , which, as is known from linear absorption, directly determines

the strength of the exciton resonance. Since the exciton strength is inversely proportional to  $a_B^d$  ( $d$  is the dimension), a decrease in Bohr radius enhances the exciton strength and competes with the Phase Space Filling reduction. Our approach also allows us to study the effect of the pump on the exciton strength for short pulse durations, where the adiabatic limit does not apply, and compare it to the Fermi Edge Singularity.<sup>16,27,15</sup> This and other applications will be discussed elsewhere.

#### D. Exciton–exciton interactions

In this section, we obtain the equation for the correlation function  $\Sigma_{xx}(n'm'\mathbf{q}'; n; t)$  which determines the renormalization of the parameters in the effective Hamiltonian and the transition matrix elements.

As can be seen from Eq. (58), the time dependence of  $\Sigma_{xx}(n'm'q'; n; t)$  is determined by the operator  $\Sigma_{xx}^\dagger(t)$ . In order to understand which processes contribute to  $\Sigma_{xx}(n'm'\mathbf{q}'; n; t)$ , it is useful to present  $\Sigma_{xx}^\dagger(t)$ , defined by Eq. (28), in second–quantized form:

$$\Sigma_{xx}^\dagger(t) = \sum_{(n,m) \neq (0,0)} \frac{1}{(n+1)! n! (m+1)! m!} \Sigma_{nm}^\dagger(t), \quad (73)$$

where the operator

$$\begin{aligned} \Sigma_{nm}^\dagger(t) = \sum_{\{\mathbf{p}\mathbf{p}'\mathbf{k}\mathbf{k}'\}} \Sigma_{nm} [\{\mathbf{p}'; \mathbf{k}'; \mathbf{k}; \mathbf{p}\}; t] & a_{\mathbf{p}_1}^\dagger \cdots a_{\mathbf{p}_{n+1}}^\dagger b_{-\mathbf{k}_1}^\dagger \cdots b_{-\mathbf{k}_{m+1}}^\dagger \\ & \times b_{-\mathbf{k}_m} \cdots b_{-\mathbf{k}_1} a_{\mathbf{p}_n} \cdots a_{\mathbf{p}_1} \end{aligned} \quad (74)$$

describes the photoexcitation of a single  $e$ – $h$  pair accompanied by its Coulomb interactions with  $n$  additional photoexcited or Fermi sea electrons and  $m$  additional photoexcited valence holes.

Substituting Eqs. (74) and (73) into Eq. (20), one can see that  $\Sigma_{nm}^\dagger(t)$  couples only to  $\Sigma_{n-1m}^\dagger(t)$  and  $\Sigma_{nm-1}^\dagger(t)$  but not to terms with higher  $n$  or  $m$ . This defines an iterative scheme for obtaining successively higher amplitudes. As a result, in undoped semiconductors, only a *finite* number of low–order terms  $\Sigma_{nm}^\dagger(t)$  contribute to the nonlinear optical response to a given order in the optical fields. For example, only the following interaction terms contribute to the third–order nonlinear polarizations:  $\Sigma_{10}^\dagger(t)$  (describing interactions between the photoexcited  $e$ – $h$  pair and an additional electron),  $\Sigma_{01}^\dagger(t)$  (describing interactions between the photoexcited  $e$ – $h$  pair and an additional hole), and  $\Sigma_{11}^\dagger(t)$  (describing interactions between the photoexcited  $e$ – $h$  pair and an additional electron and hole). Thus, a calculation of the third–order nonlinear polarization requires the solution of a four–body problem. Higher–order interaction terms do not contribute because the corresponding  $\Sigma_{nm}^\dagger(t)$  give zero when acting on states with up to two  $e$ – $h$  pairs.

We now derive the equation for  $\Sigma_{xx}(n'm'\mathbf{q}'; n; t)$ , which is more convenient for describing the above processes in the case of excitons. Starting from the definition Eq. (58), using Eq. (28) for  $\Sigma_{xx}^\dagger(t)$ , and going to the basis of exciton eigenstates of  $H$ , we obtain after some algebra

$$\begin{aligned}
\Sigma_{xx}(n'm'\mathbf{q}'; n; t) &= -\frac{i}{\hbar} \int_{-\infty}^t dt' e^{-i(\Delta\Omega - E_{n0})(t-t')/\hbar} \\
&\times \sum_{n''m''\mathbf{q}''} G(m'n'\mathbf{q}'; m''n''\mathbf{q}''; t-t') v(\mathbf{q}'') F_{nn''}(\mathbf{q}'') \\
&\times \sum_{\mathbf{k}'} [P_x(\mathbf{k}', t') - P_x(\mathbf{k}' - \mathbf{q}'', t')] \phi_{m''}^*(\mathbf{k}' - \beta\mathbf{q}'')
\end{aligned} \tag{75}$$

where

$$F_{nm}(\mathbf{q}) = \sum_{\mathbf{k}} [\phi_n(\mathbf{k} + \mathbf{q}) - \phi_n(\mathbf{k})] \phi_m^*(\mathbf{k} + \beta\mathbf{q}) \tag{76}$$

and  $G(m'n'\mathbf{q}'; m''n''\mathbf{q}''; t)$  is the two-exciton Green function<sup>29,14</sup> defined as

$$G(m'n'\mathbf{q}'; m''n''\mathbf{q}''; t) = \langle 0 | B_{n',\mathbf{q}'} B_{m',-\mathbf{q}'} B_{m'',-\mathbf{q}''}^\dagger(t) B_{n'',\mathbf{q}''}^\dagger(t) | 0 \rangle, \tag{77}$$

with  $B_{m,\mathbf{q}}^\dagger(t) = e^{-iHt} B_{m,\mathbf{q}}^\dagger e^{iHt/\hbar}$ . Thus, the problem of calculating the effective parameters is reduced to the two-exciton Green function Eq. (77) with the “bare” Hamiltonian  $H$ . The Dyson equation for  $G$  can be obtained in a straightforward way starting from the equations of motion for the exciton Heisenberg operators

$$\begin{aligned}
G(m'n'\mathbf{q}'; mn\mathbf{q}; t) &= e^{-\frac{i}{\hbar}(E_{n,-\mathbf{q}} + E_{m,\mathbf{q}})t} \langle 0 | B_{n',\mathbf{q}'} B_{m',-\mathbf{q}'} B_{m,-\mathbf{q}}^\dagger B_{n,\mathbf{q}}^\dagger | 0 \rangle \\
&+ \frac{1}{i\hbar} \int_0^t dt' e^{\frac{i}{\hbar}(E_{n,-\mathbf{q}} + E_{m,\mathbf{q}})(t'-t)} \\
&\times \sum_{m'',n'',\mathbf{q}''} V_{n''m''}^{nm}(\mathbf{q}'' - \mathbf{q}) G(m'n'\mathbf{q}'; m''n''\mathbf{q}''; t'),
\end{aligned} \tag{78}$$

where  $V_{n'm'}^{nm}(\mathbf{q}) = v_{\mathbf{q}} F_{nn'}(\mathbf{q}) F_{mm'}(-\mathbf{q})$  is the exciton-exciton interaction potential.

The Hartree-Fock approximation corresponds to retaining only the first term in the rhs of Eq. (78). Substituting the latter into Eq. (75) and using our previous results for the effective transition matrix element and Hamiltonian parameters, one obtains the contribution to the nonlinear polarization that is of first order in the exciton-exciton interaction. It can be seen that, in this case, only two-exciton states with zero center-of-mass momentum contribute to the nonlinear polarizations. The correlation effects due to exciton-exciton scattering involving the exchange of center-of-mass momentum are described by the second term in the rhs of Eq. (78). To lowest order in the exciton-exciton interaction, these can be obtained by solving Eq. (78) iteratively. This is equivalent to a second- or higher-order Born approximation to the self-energy that determines the effects of the exciton-exciton interactions on the nonlinear optical polarization. In the case where opposite-spin excitons are photoexcited, Eq. (78) can also be used to study the effects of bound biexciton states.

As can be seen from Eq. (75), the two-exciton Green function acts as a memory kernel that determines the effective parameters at time  $t$  in terms of the linear polarization at earlier times. If one only retains the first term on the rhs of Eq. (78) (Hartree-Fock approximation), such memory effects decay exponentially as determined by the dephasing time. The significance of the correlation term in Eq. (78) is that, under certain conditions, the memory kernel can become non-exponential (non-Markovian memory effects). The importance of such effects for short pulse excitation will be discussed elsewhere. Note here that in the case of monochromatic excitation, for which  $\Sigma_{xx}^\dagger$  is time-independent, the correlations simply change the magnitude of the various parameters.

## VI. FOUR-WAVE-MIXING POLARIZATION

Let us now turn to the polarization along the four-wave-mixing direction,  $\mathbf{k}_3 = 2\mathbf{k}_p - \mathbf{k}_\tau$ . The latter can be obtained by substituting Eqs. (48) and (49) into Eq. (41) and retaining only terms proportional to  $e^{i\mathbf{k}_3\mathbf{r}}$ . After some algebra, we obtain

$$P_{\text{FWM}}(t) = \frac{i\mu}{\hbar} e^{i\mathbf{k}_3\mathbf{r} - \omega_p(t-\tau)} \int_{-\infty}^t d\tau(t') \langle 0 | [U\mathcal{U}(t', t) U_{\text{FWM}}^\dagger(t) - (t \leftrightarrow t')] | 0 \rangle, \quad (79)$$

where

$$U_{\text{FWM}}^\dagger(t) = U W_{\text{pp}}^\dagger(t) - \Sigma_x^\dagger(t) U \Sigma_x^\dagger(t), \quad (80)$$

and

$$W_{\text{pp}}^\dagger(t) = \frac{1}{2} [\Sigma_1^\dagger(t)]^2 - \Sigma_2^\dagger(t), \quad (81)$$

is the “irreducible” biexciton operator satisfying

$$i\hbar \frac{\partial}{\partial t} W_{\text{pp}}^\dagger(t) | 0 \rangle = H W_{\text{pp}}^\dagger(t) | 0 \rangle - \frac{d_p(t)}{2} U^\dagger \Sigma_x^\dagger(t) | 0 \rangle. \quad (82)$$

In the above, we used the fact the  $\Sigma_{\text{xx}}^\dagger(t) | 0 \rangle = 0$ . Thus, the four wave mixing polarization is determined by  $\Sigma_x(t)$ , which describes the linear pump-induced polarization, and the biexciton transition operator  $W_{\text{pp}}(t)$ , which includes all exciton-exciton interaction effects in the four-wave-mixing signal. One can express  $W_{\text{pp}}^\dagger(t) | 0 \rangle$  in terms of the two-exciton Green function Eq. (77) by following the procedure of the previous section. Note here that, unlike for the pump-probe polarization, the pump-induced corrections to the Hamiltonian do not contribute to the third-order polarization along the direction  $\mathbf{k}_3$ . Therefore, the  $\chi^{(3)}$  calculations of the four-wave-mixing signal neglect the optically-induced change in the time evolution operator  $\mathcal{U}(t, t')$ , while similar pump-probe calculations include this effect only to first order in perturbation theory. As discussed in the previous section, such calculations do not properly treat the shift of the exciton resonance and neglect the memory effects and quantum dynamics induced by the interactions in  $H_{\text{eff}}(t)$ . The latter are especially important in the case of the Fermi-edge singularity.<sup>16</sup>

Finally, let us discuss the connection between our approach and other works. In Refs. 13 and 14, it was shown that the third-order nonlinear polarization can be expressed exclusively in terms of single-pair and two-pair creation operators, corresponding to our  $\Sigma_x^\dagger(t)$  and  $W_{\text{pp}}^\dagger(t)$ . Similarly, one can obtain  $\chi^{(3)}$  along the four-wave-mixing direction by simply replacing  $H_{\text{eff}}(t)$  in Eq. (79) by  $H$ . The connection to Ref. 14 can be established by noting that  $\langle \alpha 2 | W_{\text{pp}}^\dagger(t) | 0 \rangle$  coincides with the lowest term in the expansion of the Hubbard operator  $| 0 \rangle \langle \alpha 2 |$ . Furthermore, by projecting Eq. (82) into two-pair states, one can identify the amplitude  $\langle 0 | b_{-\mathbf{k}} b_{-\mathbf{k}'} a_{\mathbf{k}'+\mathbf{q}} a_{\mathbf{k}+\mathbf{q}} W_{\text{pp}}^\dagger(t) | 0 \rangle$  with the four-point density matrix introduced by Axt and Stahl.<sup>13</sup> This connection is less obvious for our pump-probe results, Eqs. (50) and (51). The reason is that, as discussed above, these include important contributions beyond  $\chi^{(3)}$ . However, by only keeping the lowest term in a perturbative expansion of the time-evolution operator [i.e., by restricting to  $\chi^{(3)}$ ], one can obtain after straightforward but laborious algebra the expression for the pump-probe polarization exclusively in terms of

$$\Sigma_j^\dagger(t)|0\rangle = \frac{i}{\hbar} \int_{-\infty}^t dt' d_j(t') e^{-iH(t-t')/\hbar} U^\dagger |0\rangle, \quad (83)$$

and

$$W_{ij}^\dagger(t)|0\rangle = \frac{i}{\hbar} \int_{-\infty}^t dt' d_i(t') e^{-iH(t-t')/\hbar} U^\dagger \Sigma_j^\dagger(t')|0\rangle, \quad (84)$$

with  $i,j=p,\tau$ . The corresponding expression is rather tedious and is omitted here. By comparing Eq. (83) to Eqs. (21) and (23), it can be seen that  $\Sigma_p^\dagger(t)|0\rangle = \Sigma_x^\dagger(t)|0\rangle$ . It can also be seen from Eq. (84) that  $W_{pp}^\dagger(t)|0\rangle$  coincides with the solution of Eq. (82). The third-order polarization is thus determined by the states  $W_{ij}^\dagger(t)|0\rangle$ , which, for  $i \neq j$ , describe the effects of the interference between the pump and the probe.

## VII. CONCLUSIONS

In conclusion, we discussed a general theoretical approach for describing Coulomb many-body effects in the ultrafast coherent dynamics in semiconductors and metals. Our approach provides a complete description of the correlation and non-Markovian memory effects by reducing the calculation of the nonlinear optical response of the “bare” system onto the linear response of a “dressed” system described by the effective time-dependent Hamiltonian, Eq. (65). Furthermore, it allows us to study the coherent ultrafast nonlinear optical response of Fermi sea systems.<sup>16</sup>

As is known,<sup>6</sup> the calculations of the third-order nonlinear polarizations starting from equations of motion must address the time evolution of exciton and biexciton states. In view of the unresolved numerical problems facing a straightforward calculation of biexcitonic effects (except in one dimension), our approach has the advantage of providing a physically-intuitive picture for viewing their manifestations in the ultrafast nonlinear optical response. Close to the exciton frequency, these effects can be taken into account via the renormalization on the electron/hole dispersions and interaction potential as well as the probe-induced optical transition matrix elements. Our approach also allows us to treat the Coulomb-induced quantum dynamics arising from the semiconductor response to such perturbations, which cannot be captured within the  $\chi^{(3)}$  approximation. Note that, for monochromatic excitation, the exciton-exciton correlations simply change the magnitude of the effective parameters, while for ultrashort pulses they also affect their time-dependence over times comparable to the dephasing time.

Our theory separates the effects due to the renormalization of the electron/hole dispersions and interaction potential from the renormalization of the probe-induced optical transition matrix elements. These affect the nonlinear polarization in a different way, as can already be seen in the absence of Coulomb interactions by recalling the well-known “dressed atom” results for a two-level system.<sup>22</sup> In the latter case, the shift in the energies results in an overall resonance shift (e.g., ac-Stark effect) which cannot be correctly described within  $\chi^{(3)}$  calculations. Such effects are described here by the time evolution operator for the effective Hamiltonian  $H_{\text{eff}}(t)$ . In semiconductors, the additional quantum dynamics (not captured by  $\chi^{(3)}$ ) arising from the non-commutativity of the effective Hamiltonian at different times can be simply described with the Schrödinger equation for the effective exciton Hamiltonian

$H_{\text{eff}}(t)$ . On the other hand, the renormalization of the transition matrix elements, due to Phase Space Filling and, in semiconductors, exciton–exciton interaction effects, leads to an overall factor in the polarization that can be calculated to third–order in the optical fields.

Thus our theory identifies a number of competing physical processes, each leading to different nonlinear dynamics and spectral features. In undoped semiconductors, we can obtain the parameters determining the strength of the above nonlinearities in terms of the “bare” semiconductor one– and two–exciton Green functions. Finally, we also established a connection between our approach and  $\chi^{(3)}$  calculations in undoped semiconductors. We believe that the present theory is well-suited for interpreting the physics conveyed by ultrafast coherent nonlinear optics experiments in semiconductors and metals using pulses as short as 10 fs.

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